RESEARCH ARTICLE

Corrosion Inhibition of Copper by Olive Leaves Extract as Environmentally Friendly Inhibitors in Acidic Media

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Abstract

An inhibition effect of olive leaves extract in corrosion of copper alloy in hydrochloric acid solution was studied by means of potentiodynamic polarization and scanning electron microscopy *(SEM)*. The inhibition efficiency has as inhibitor concentration increased but decreased with increase in temperature. Fallouts have depicted that the inhibition takes place throughout adsorbing inhibitor molecules on the metal surface that agrees with Langmuir adsorption isotherm. Several thermodynamic parameters $(\Delta G_{ads.})$ in addition to activation energy (E_a) have been determined to explain the process of corrosion inhibition. The measurements of polarization indicated that olive leaves extract is of cathodic type. The surface characteristic of the inhibited and uninhibited metal tasters have examined by SEM.

Keywords: *Corrosion inhibition, copper, olive leaves extract, Adsorption Mechanism thermodynamic parameters.*

Introduction

Corrosion is a natural phenomenon that is exposed to any metal in certain conditions to return to its original state at equilibrium [1].Corrosion is also known as damage of metals and their alloys as a result of chemical or electrochemical reactions with the surrounding environment. Metallic materials suffer more than other processes of corrosion, as the properties of the material change and gradually decrease into compounds such as (oxides, sulfates, carbonates) [2]. Cu and its alloys corrode with materialization of oxides layers (patina). Nevertheless, these oxides layers tends for degradation at what time exposed to contaminated atmosphere [3].

However, the use of chemical inhibitors such as chromates, nitrates, carbonates, phosphates, silicates and other toxic compound as corrosion control inhibitors have proved to be effective inhibitors at relatively low cost but these chemicals create more problems than the solution they offer [4].Plant extracts are being relevant as corrosion inhibitors for somewhat lengthy period as can be observed from the reported studies in the literature. Natural inhibitors are particularly interesting because they are inexpensive and have no threat to the environment, The natural-occurring substances contain of many natural organic compounds such as pigments, flavonoids, ascorbic acid etc. the extracts of these substances constitute of nitrogen, oxygen and sulfur-containing compounds which make them good and effective anti-corrosion inhibitors [5, 8]. inhibitors generally contain heterogeneous atoms such as (N, O, S) which have been found to have electronic densities suitable for acting as an antidote to corrosion an (N, O, S) are the active center of the adsorption process on the metal follows the inhibitory efficiency of P>S>N>O [9].The olive tree is an evergreen tree and has the ability to withstand harsh environmental.

Man has dealt with this tree since the beginning of the ages, relying on the oil of fruits because of its economic importance and food. The active compounds in olive tree leaves were extracted by many researched as they were found to contain a group of active compounds through the use of a technical measure GC-MS (gas chromatography mass spectrometry) [10].

The highest percentage of these compounds was compounds for turbines, essential oil, alkaloids, phenol compounds, alorubin and

other compounds. The phenolic complexes have been extracted from olive leaves varieties consisting of gallic acid, caffeis acid, vanillic acid, P-hydroxy benzoic acid, and syringic acid [11]. The objective of this paper is to examine the influence of olive leaves extract as new ecologically responsive corrosion inhibitor for Cu in hydrochloric acid solution by using electrochemical polarization method.

Olive Leaves Extraction

Olive leaves have been gathered from the Olive trees in Baghdad and then washed and left it for 3 days in the oven at 80 °C to dry. The dried leaves are thoroughly grinded using an electric grinder to get a fine powder. The powder was sifted using (90 µm × 17 cm) sieves. Then take 25 gm of Olive powder in 400 ml of 0.5M HCL and heated the mixture for 10 minutes then leave it cooled in room temperature and out of light. Filter the mixture with filter paper, then take different concentrations (50,100,200 and 400) ppm of stock solution.

Techniques used in Research

- *X-Ray Diffraction (XRD)* In this study we determine the percentage of the

components found in the alloys, where it was found that the proportion of copper (99%) and (1%) impurities. means that the alloy is a copper high purity.

- *SEM measurements* the electrode surfaces of copper were analyzed by SEM-inspect-FEI S50, Japan before and after immersion in acidic solution without and with 400 ppm of olive leaves extract at 298K.

Results and Discussion

The Potentiodynamic Polarization

The potentiodynamic polarization results of Cu alloy in hydrochloric acid solution are illustrated in Figure (1) with different concentrations of olive leaves extract. Tafel extrapolation method was used to calculate the corrosion parameters (E_{corr}), (i_{corr}) (b_c) and (b_a) from the polarization curves.

The resetting data were displayed in Table (1) and these data show that corrosion current density (i_{corr}) lessened with increasing extract concentration, the adding of olive leave extract shifts the potential with shifting the corrosion potential to more negative magnitudes that indicate this inhibitor acts as cathodic- type inhibitor.
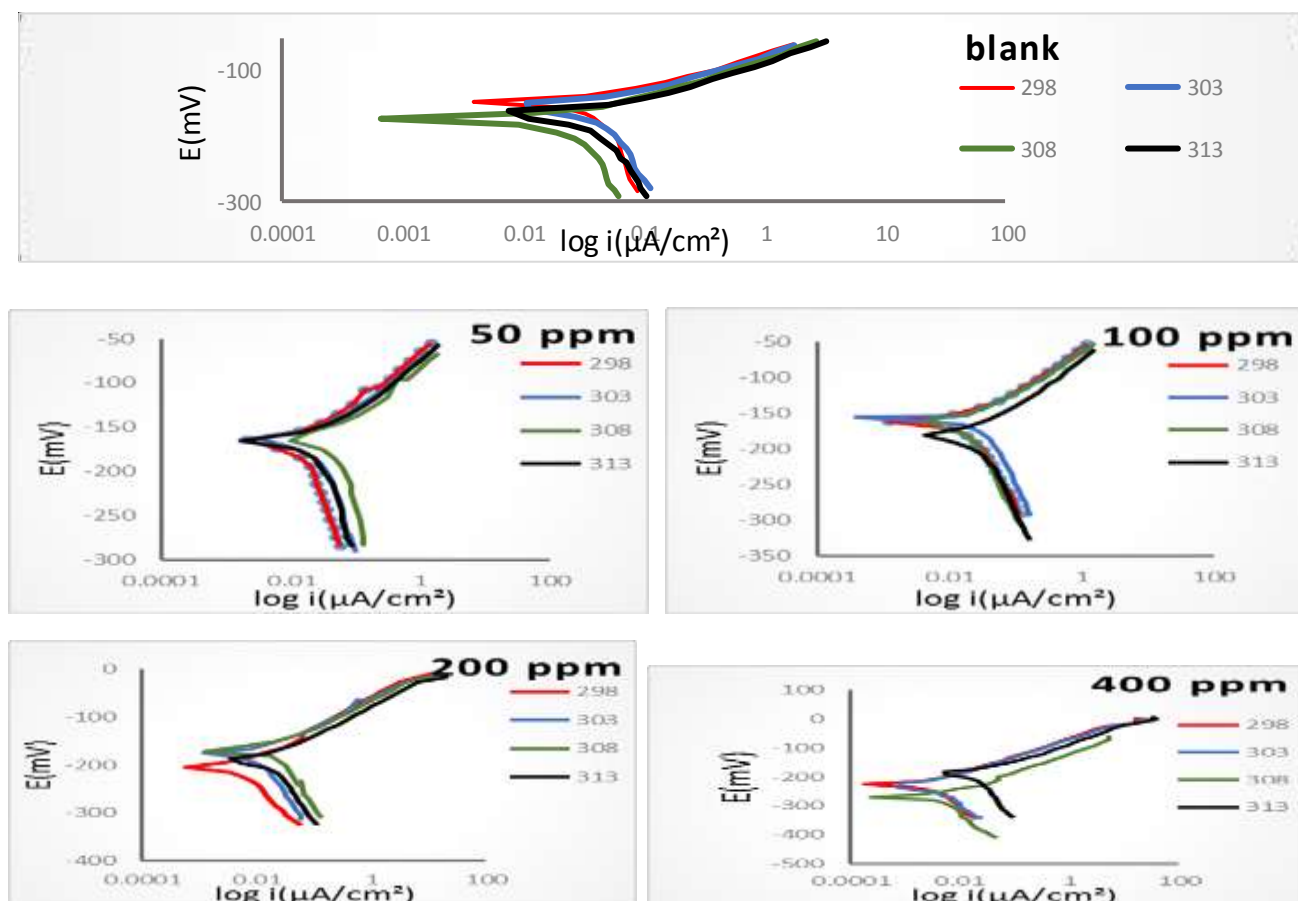

Figure 1: Polarization results for copper corrosion in acid solution (HCl) at temperature range (298-313) K and under existence of diverse concentrations of olive leaves

Table 1: Corrosion standards for Cu alloy in HCL solution over temperature range (298-313) K of different Olive leaves

Conc.ppm	i_{corr} ($\mu A.cm^{-2}$)	$-E_{corr}$ mV	$+b_a$ ($mV.dec^{-1}$)	$-b_c$ ($mV.dec^{-1}$)
blank	☐☐	☐☐☐☐☐☐	☐☐	☐☐☐☐
50	11.2	-167	49	-130
100	10	-164	44	-78
200	4.1	-206	62	-109
400	1.6	-226	50	-79

Activation Energy of Copper Corrosion

The activation energy is calculated for corrosion process of Cu in hydrochloric acid under nonexistence and existences of inhibitors have evaluated from Arrhenius equation [12, 13]. As shown in equation:

$$\log i_{corr} = \frac{-Ea}{2.303RT} + \log A \dots (1)$$

Where (Ea) stands for the energy of activation, (R) stands for the gas constant (8.314) and (A) stands for Arrhenius constant. Equation (2) predicts that plotting of in (i_{corr}) versus $\frac{1}{T}$ should be linear as we tentatively detected. The slope of the line offers $= \frac{-E^*}{RT}$, but the intercepting of the line generalized to $\frac{1}{T} = o$ gives l n A. Through the use of alternative form of Arrhenius relationship (ΔH) and (ΔS) can be obtained where:

$$\ln\left(\frac{i_{corr}}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{act}}{R}\right) - \left(\frac{\Delta H_{act}}{RT}\right) \dots (2)$$

Where (h) stands for "planks constant"(6.626*10^{-34} J.S), (N) is "Avogadro's number" (6.022*10^{23} mol^{-1}), it is possible to draw $(\ln \frac{i_{corr}}{T})$ vs. $(\frac{1}{T})$, where the slope of the straight line shows its magnitude $(-\frac{\Delta H_{act}}{R})$ and the intersection shows its value$(ln\frac{R}{Nh} + \frac{\Delta S_{act}}{R})$. As shown in the Figures (2-3).The results shown in Table (2):
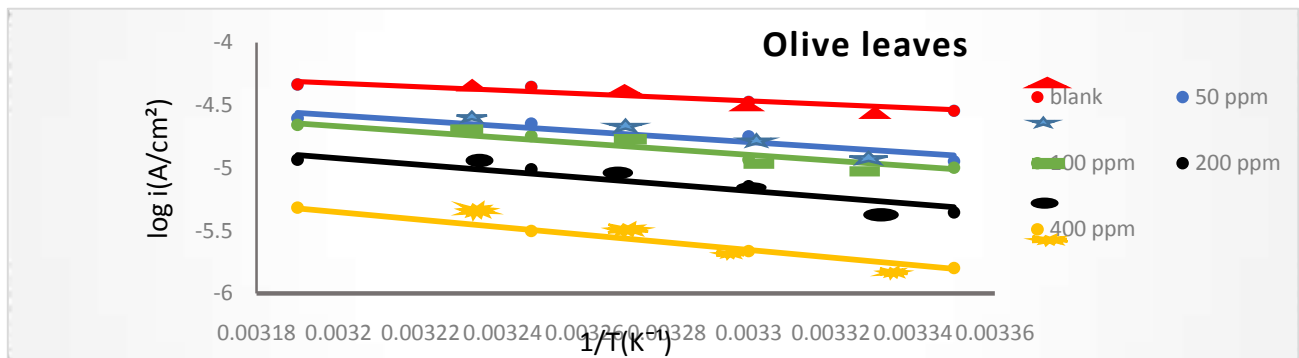

Figure 2: Charts of Arrhenius of log I$_{corr}$ versus 1/T for the corrosion of Cu in 0.5 M HCl with diverse concentrations of olive leaves extract
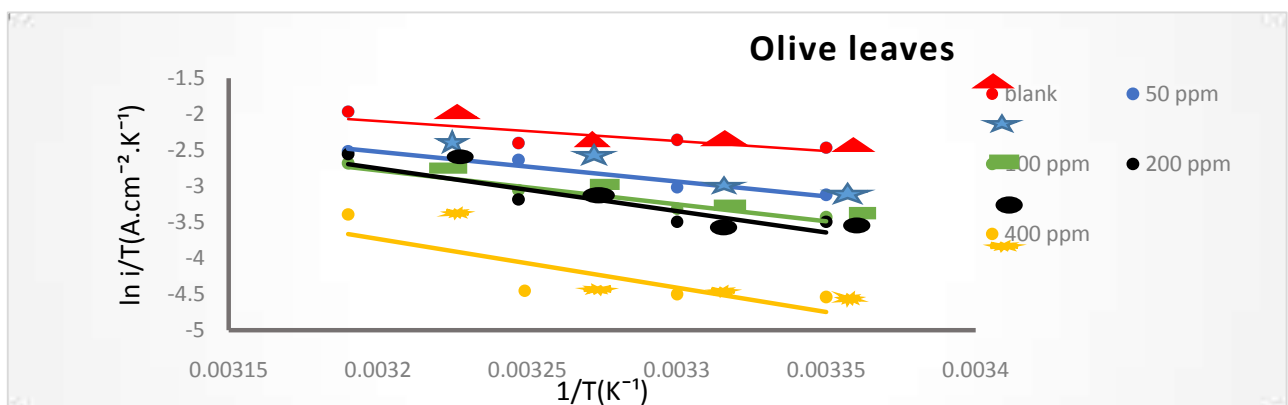

Figure 3: Charts of Arrhenius of ln (icorr/T) versus 1/T for the copper corrosion in 0.5 M HCl with dissimilar concentrations olive leaves extract.

Table 2: Activation energy (Ea), activation enthalpy (ΔHa), and the entropy of activation (ΔSa) for the corrosion of copper in 0.5 M HCl and in the presence of inhibitor

Conc. (ppm)	E_a (KJ. mol^{-1})	A (molecules.cm^{-2}.s-1)	$-\Delta S_a$ (J.K^{-1}.mol^{-1})	ΔH_a (KJ. mol^{-1})
Blank	26.6	7.98×10^{23}	244.2	26.6
50	40.3	8.62×10^{25}	238.2	29.5
100	43.5	2.41×10^{26}	230.4	32.6
200	49.7	1.48×10^{27}	214.9	40.2
400	57.7	1.17×10^{28}	176.9	52.3

The increase in the activation energy (Ea) of the Arhinius coefficient is stabilized indicates a high reaction rate, while the decrease in the activation energy indicates of the Arhinius coefficient is stabilized indicates a low reaction rate. There is also a clear difference in the values of the activation energies and the Arhinius coefficient where the corrosion reaction begins with sites that have low activation cards and then spread to the sites that have higher activation energies [14].This means that the addition of the inhibitors upsurges the energy barrier of Cu corrosion in the solution containing chlorine ions, and that the corrosion process will also occur and that the inhibitors delays it. In addition, the increase in temperature increasing corrosion process and then lessens the efficiency of inhibition, where increase in inhibitor concentration causes increase of the density of electrons in the adsorping centres of the inhibitor molecules that leads to improved the efficiency of inhibition [15].

Inhibition Efficiency (IE %) and Surface Coverage (θ):

The inhibition efficiency (IE %) are calculated by using the relation [16]

$$IE\% = \left[1 - \frac{i^\circ}{i}\right] \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

In general, and $i\circ$ stand for corrosion current densities in nonexistence and occurrence of inhibitors in the corrosion medium correspondingly. And the surface coverage (θ) is evaluated through [17] as explained in Table (3).

$$\theta = \frac{IE\%}{100} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Table 3: Inhibition efficiencies (IE %) and surface coverages (θ) of Olive leaves under numerous concentration with temperature range (298-313) K in 0.5M HCL.

T. K	Con. Ppm							
	50		100		200		400	
	IE%	θ	IE%	θ	IE%	θ	IE%	θ
298	65	0.65	68.4	0.684	87.2	0.872	95	0.95
303	40.2	0.402	60.7	0.607	74.9	0.749	93.8	0.938
308	39.7	0.397	52.6	0.526	66.1	0.661	90.7	0.907
313	38	0.38	52.2	0.522	65.2	0.652	76.6	0.766

The above consequences showed that the efficiency of inhibition has been inversely proportional to the temperature where the uppermost efficiency was (298), and also found that the Olive leaves provided a high efficiency where the inhibitory efficiency (IE %) in (298) K for Olive is (95%)

The IE% magnitudes were found to be augmented with increasing the concentration of the inhibitors and reduction with increasing temperature [18]. Along with the surface coverage data have an imperative role in the evaluation of the features of inhibitors and it is advantageous when discussing adsorption properties with the benefit of isotherm adsorption as it can be described with additions of inhibitor molecules that are on the surface in the metal and interact with them [19].

The Adsorption Isotherm

The surface coverage (θ) of working electrode for Cu surface by the inhibitor (olive leave extract) and the concentration of inhibitor solution (C_{inh}) have been investigated by fitting to numerous adsorbing isotherms.

The finest fit has gotten with Langmuir isotherm that is given by [20, 21] as shown in Figure (4).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{adc}} + C_{inh} \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Where, K_{ads} stands for the equilibrium constant of the adsorbing / desorbing processes, and it reveal the kinship of inhibitor molecules concerning surface adsorbing positions.From calculated magnitudes of K$_{ads}$. The Gibbs free energy of adsorbing has been evaluated by [22]:

$\Delta G^{\circ}{}_{ads} = -RTln\ (55.5K_{ads})$ .... (6)

R denotes for gas constant, T denotes for absolute temperature and (55.5) magnitude denotes the molar concentration of water in mol/L.

The standard enthalpy of adsorbing is feasibly calculated based on van 't Hoff formulation;

$\ln K_{ads} = -\dfrac{\Delta H_{ads}}{RT} + constant$ .... (7)

A chart of ln K$_{ads}$ magnitudes vs. 1/T magnitudes provides a straight line and the

slope of the straight line is equal $\dfrac{-\Delta H_{ads}}{R}$. The negative magnitudes of ΔH° discloses that the adsorbing of olive leaves extract molecules is an exothermic process. The magnitudes of $\Delta G^{\circ}{}_{ads}$ in the existence of the inhibitor are negative that is gone with exothermic adsorbing process. $\Delta S^{\circ}{}_{ads}$ of inhibition process can be computed from equation [23]. The above results are as in Table (4):

$\Delta S^{\circ}{}_{ads} = \dfrac{\Delta H^{\circ}{}_{ads} - \Delta G^{\circ}{}_{ads}}{T}$ ....
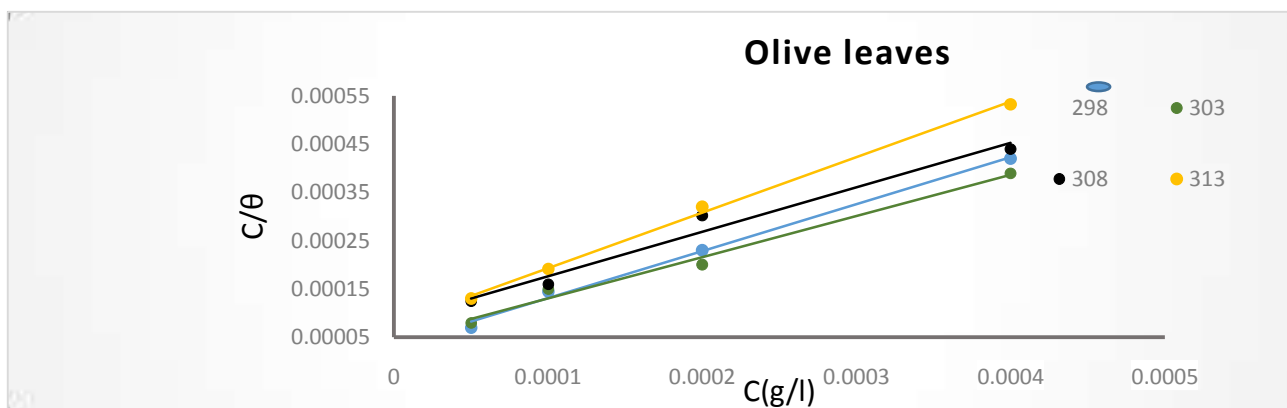(8)

Figure 4: Isotherm plots of Langmuir for the (Olive leaves extract) adsorption on copper in 0.5 HCL

Table4: Thermodynamic parameter for adsorption of Olive leaves on copper in 0.5 M HCl

T K	K$_{ads}$ (g^{-1}.L)	-$\Delta G^{\circ}{}_{ads}$ (kJ.mol^{-1})	-$\Delta H^{\circ}{}_{ads}$ (kJ.mol^{-1})	$\Delta S^{\circ}{}_{ads}$ (J.K-1.mol^{-1})
298	20000	34.4		0.04194
303	16666	34.6		0.04191
308	14286	34.8	21.9	0.04188
313	12500	35		0.04185

ΔG_{ads} magnitudes up to -20kJ/mol have presumed as the electrostatic interacting among charged molecules besides charged metal surface (physisorption). Whereas ΔG_{ads} magnitudes have been higher negative as compared with -40kJ/mol that stand for charge transfer or sharing from inhibitor molecules to metal surface for producing a coordinate covalent bond (chemisorption).

ΔG_{ads} magnitudes in this paper have been within (34.4-35) kJ.mole^{-1}, that means the adsorbing of this inhibitor onto Cu alloy surface takes place throughout physical and chemical adsorption [24].The negative magnitudes of (ΔH°) points to that the adsorbing process of the inhibitor molecules stands for an exothermic process .The adsorption is expected to be physical or chemical, while positive magnitude reveals that it's an endothermic process which attributed to chemisorption.

Subsequently, the adsorbing of the plant extracts molecules on the Cu surface obtained in this paper the refers to chemisorptions [25].

Scanning Electron Microscope (SEM) Measurements

SEM experimentations have done to prove if the extract molecules are in fact adsorbed on copper alloy surface or just peeled off the surface. The SEM micrographs for Cu alloy surface after immersion in 0.5 mol.dm^{-3} of hydrochloric acid regardless or with insertion of the optimum concentration of olive leave extract as shown in figure (5) Where it is shown in figure (a) polished copper alloy, (b) shown Cu alloy immersed in hydrochloric acid (HCL), and (c) shown copper alloy in (0.5) M (HCL) solution in existence of 400 ppm of olive leaves extract. It can be noticed from comparison of SEM micrographs

obtained in the nonexistence and in existence of the extract reveals a good inhibiting effect of this compound.
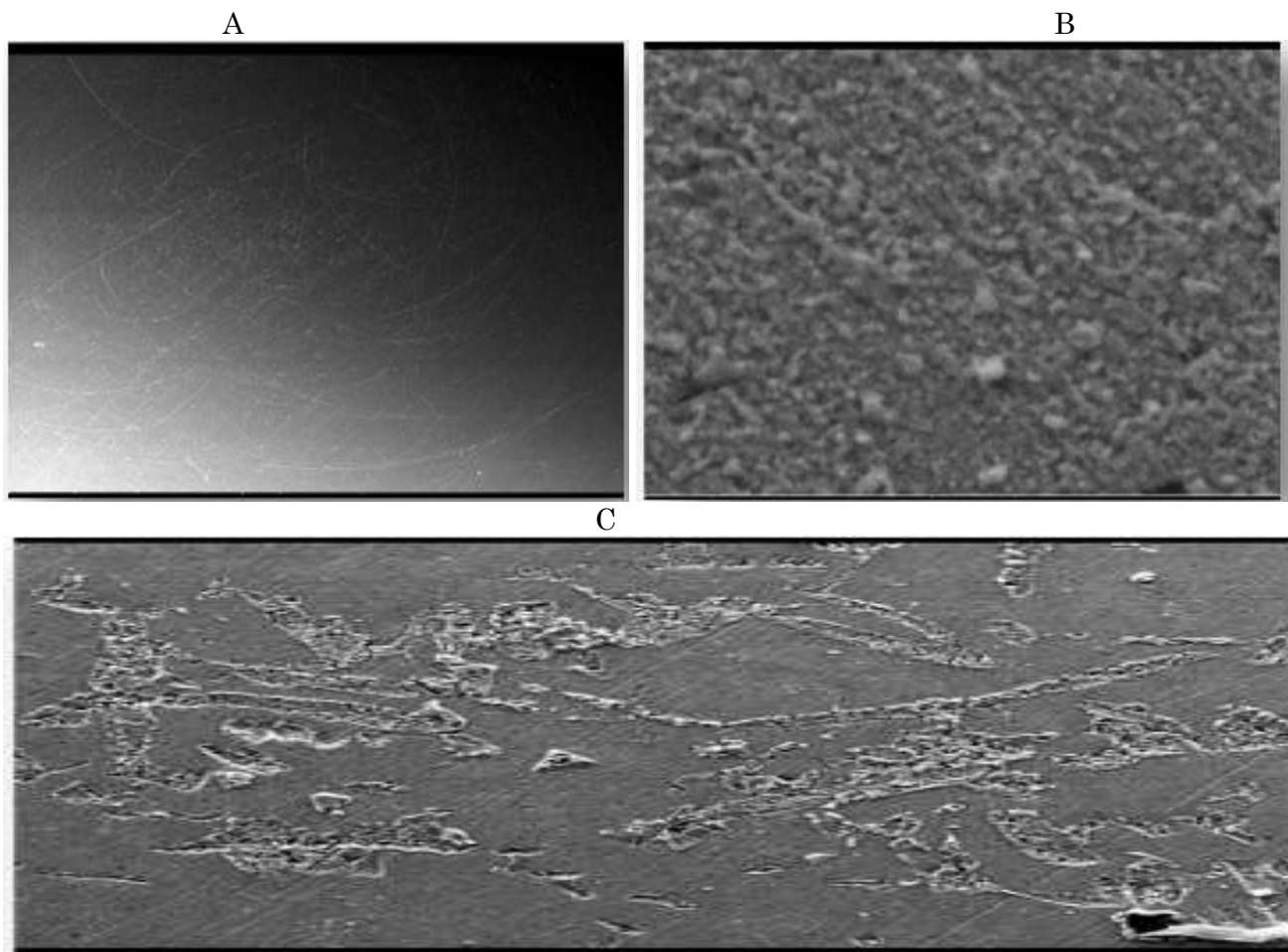
A

B

C

Figure 5: Micrographs of scanning electron

Conclusions

Through the results the following conclusions was deduced

- The rate of corrosion of Cu alloy in hydrochloric acid depends largely on temperature and especially at high temperatures.

- Olive leaves extract works as an in effect inhibitor for Cu corrosion.

- The inhibitory efficacy of the extract depends on the concentration of the inhibitor where efficiency was obtained (95%) at the concentration (400) ppm.

- The magnitudes of the activation energies (E_a) are increased by growing concentration of the inhibitor and by raised temperature. The magnitudes of the activation energies (E_a) are greater with the existence of the inhibitor as compared in the nonexistence of it, indicating that the inhibitors raise the energy barrier to more values.

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